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S. C. Abrahams

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Abstract: Barium tetrasulfide monohydrate forms strongly piezoelectric crystals belonging to the orthorhombic system, space group $D_2^3 - P2_12_12$ with four molecules in the unit cell of dimensions $a = 9.67$, $b = 7.99$ and $c = 7.81 \overset{\circ}{\text{A}}$. The crystal structure has been completely determined, and the values of the 17 atomic coordinates refined by double Fourier series and least-square methods, based upon 296 terms derived from visual intensity measurements, in the three principal zones. The barium atom is completely ionized, and is in ionic contact with the sulfur atoms and the oxygen of the water molecule. The tetrasulfide ion possesses C_2 symmetry. Like the anion of cesium hexasulfide, the tetrasulfide ion is nonbranched and nonplanar, and also exhibits a similar alternation in bond length. Two kinds of sulfur-sulfur bonds are present, of length 2.02 and $2.07 \overset{\circ}{\text{A}}$, allowing a new tentative bond-order vs. bond-length curve for sulfur to be established.

The crystal structure of cesium hexasulfide has been studied previously (Abrahams and Grison, 1953) in this laboratory, during the course of an investigation of the properties of the VI_b group of the periodic table. This work unambiguously demonstrated the polysulfide chain to be nonbranched and nonplanar,

and also indicated that two kinds of bond occurred in the hexasulfide ion, of length 2.02 and 2.11 Å, the standard deviation being 0.03 Å. The present study was undertaken to determine whether a similar alternation in bond length also occurred in the tetrasulfide ion. Barium tetrasulfide is considerably more stable chemically than cesium tetrasulfide, although cesium forms the longer stable polysulfide (Schöne, 1862; Biltz and Wilke-Dörfurt, 1905). Barium tetrasulfide is reported to crystallize with varying amounts of water (Veley, 1886), but the conditions of crystallization used (Robinson and Scott, 1931) gave only the monohydrate.

The values of the dihedral angle in the hexasulfide ion were 78.8, 81.9 and 61.6°, * indicating that this angle was largely influenced by the crystallographic environment. Recently, Marsh, Kruse and McCullough (1953) have reported the dihedral angle in p,p'-dichlorodiphenyl diselenide to be ca. 74°, and Toussaint's (1945) data indicate the corresponding angle in p,p'-dibromodiphenyl disulfide to be ca. 78°. The values of these angles in the tetrasulfide ion were hence of further interest, particularly in view of Pauling's (1949) postulate that the most likely value for this angle is about 100°.

Crystal data

Barium tetrasulfide monohydrate, $\text{BaS}_4 \cdot \text{H}_2\text{O}^{**}$ forms strongly piezoelectric crystals; decomposes on melting; $D_{\text{meas}} = 3.107 \text{ gm cm}^{-3}$ (determined by flotation in methylene iodide-carbon tetrachloride); $D_{\text{calc}} = 3.120 \text{ gm cm}^{-3}$ for four molecules per unit cell; orthorhombic with $a = 9.67 \pm 0.02$, $b = 7.99 \pm 0.02$ and $c = 7.81 \pm 0.02$ Å; absent spectra, (h00) only with $h = 2n + 1$ and (0k0)

* The angles quoted by Abrahams and Grison (1953) are, in fact, all complements of the correct values.

** Analysis:

	I	II	Calc. for $\text{BaS}_4 \cdot \text{H}_2\text{O}$
H_2O	6.45%	6.52%	6.34%
Ba	48.31	48.50	48.44
S	45.20	44.90	45.21

only with $k = 2n + 1$. Space group is hence uniquely $D_2^3 - P2_12_12_1$. No molecular or ionic symmetry is required. Absorption coefficient for MoK α radiation ($\lambda = 0.7107 \text{ \AA}$) is 82 cm^{-1} , for CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) is 670 cm^{-1} . Volume of the unit cell is 603.6 \AA^3 . Total number of electrons per unit cell = $F(000) = 520$. Dielectric constant at room temperature (Westphal, 1953) is ca. 8 ± 2 in all directions.

Analysis of the structure

An examination of the intensity distribution in the $(h0\ell)$, $(hk0)$ and $(0k\ell)$ layers reveal the presence of an outstandingly strong superlattice (e.g., Fig. 1).

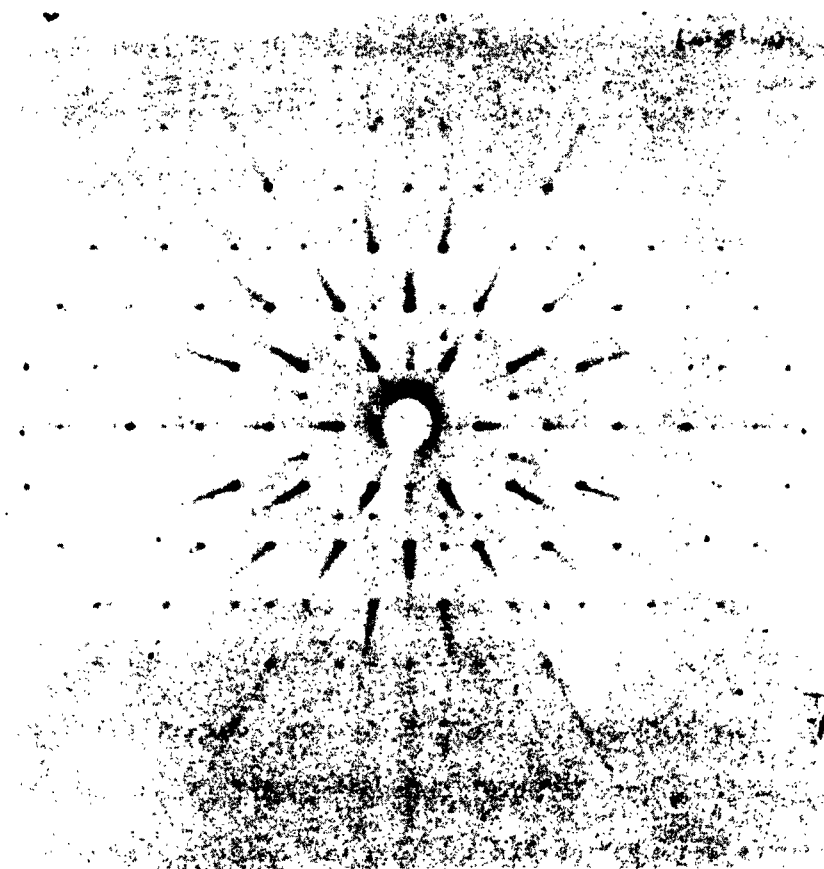


Fig. 1. Precession photograph of the $(hk0)$ layer in $\text{BaS}_4 \cdot \text{H}_2\text{O}$.

In the $(h0\ell)$ layer, reflections of the form $h = 4n$ when $\ell = 2n$, and $h = 2n + 1$ when $\ell = 2n + 1$ are very strong; in $(hk0)$, of the form $h = 4n + 2$ when $k = 2n + 1$, and $h = 4n$ when $k = 2n$; and in $(0k\ell)$ of the form $h = 2n$ when $\ell = 2n$ only are outstanding. Assuming these strong reflections are produced by barium atoms contributing fully to these planes, it is easy to show from the structure factor expressions

$$A_{hk\ell} = 4 \cos 2\pi \left(hx + \frac{h+k}{4} \right) \cos 2\pi \left(ky - \frac{h+k}{4} \right) \cos 2\pi \ell z ,$$

$$B_{hk\ell} = -4 \sin 2\pi \left(hx + \frac{h+k}{4} \right) \sin 2\pi \left(ky - \frac{h+k}{4} \right) \sin 2\pi \ell z ,$$

that the barium atoms must lie close to the coordinates $1/8, 1/4, 1/4$, retaining the origin listed in the International Tables (1952).

The method of Wilson (1942) and Harker (1948) was used to place the intensities in the $(hk0)$ layer on an absolute scale. The scale factor thus derived was finally found to be 9.2 percent too high, by comparison with the scale derived from the coordinates given in Table 1 (in the case of Cs_2S_6 the scale factor derived by this method was finally found to be 10.4 percent too high). The temperature factor B in the expression $\exp \left\{ -B[(\sin \theta)/\lambda]^2 \right\}$, assumed to be isotropic and the same for each kind of atom present, obtained by this statistical treatment was 0.75 \AA^2 , and it was not found necessary to alter this value throughout the remainder of the investigation. Structure factors, calculated for barium at $1/8, 1/4, 1/4$, with the atomic scattering factor based on the Thomas field, and the above value of B , gave a value for R_1 (defined in the usual way) of 0.19 for the strong planes. The amplitudes of the remaining planes, of course, were computed to be identically zero. This good agreement encouraged the belief that the strong reflections were primarily due to a full contribution from the barium atoms. The phases associated with these atoms were then used to compute a Fourier series on XRAC, through the kindness of Professor R. Pepinsky, using the limited set of superlattice planes only (Fig. 2). Since all other terms have

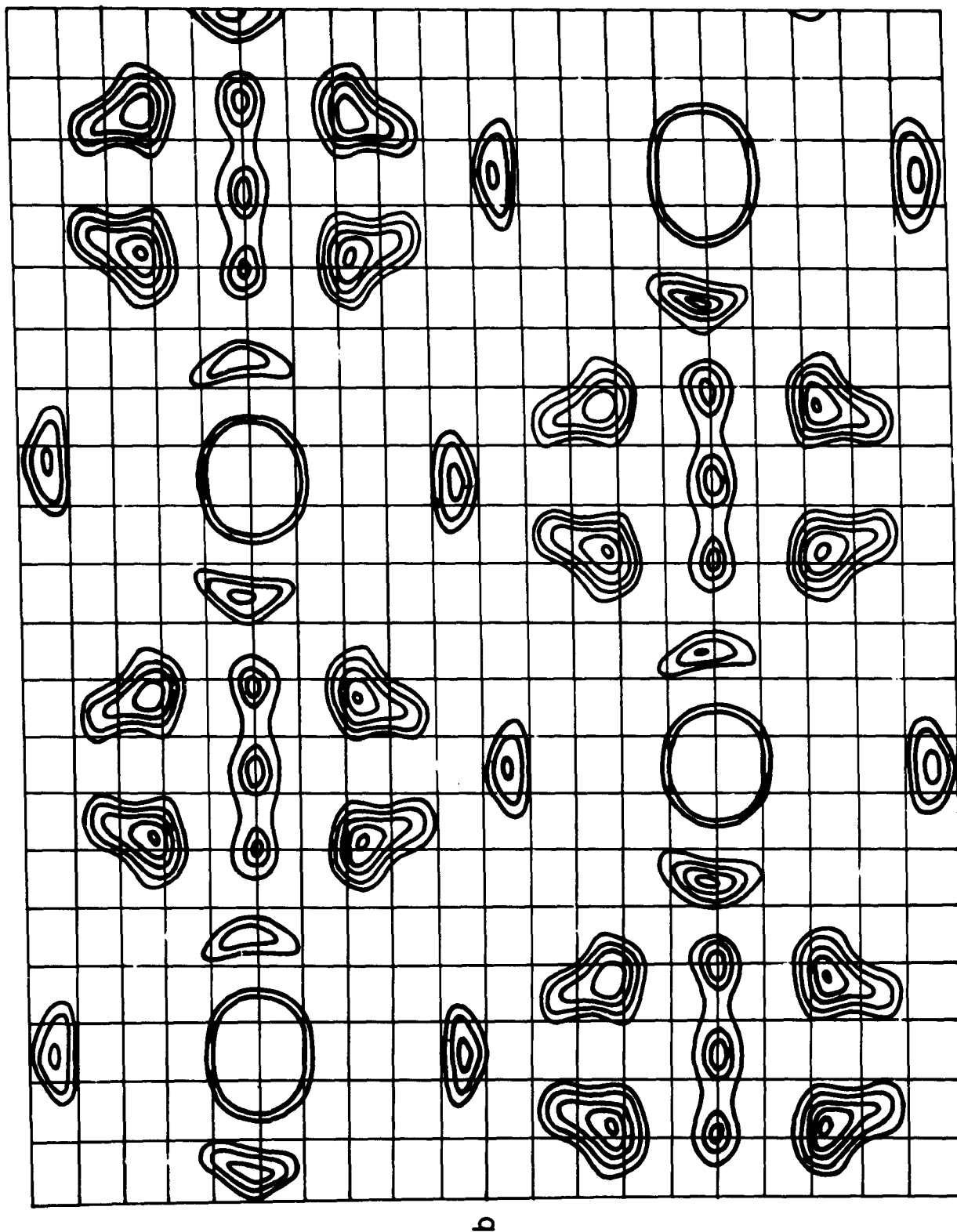


Fig. 2. Symmetrized c-axis projection, based only on the barium atom at $1/8, 1/4$, computed on the X-Ray Analog Computer.

been left out, this series gives a rather inaccurate and artificially symmetrized view of the correct electron density projection, which could be obtained with complete (hk0) data.

Attempts to desymmetrize Fig. 2 were made by introducing the next most intense reflections into the series in sets of three, with various phase combinations, using the nonnegativity of the background as criterion. This method was not very successful, primarily due to the diffraction effects of the heavy atom, which interfered with the criterion. Other efforts, based upon improving the general appearance of the projection, were also not very successful. The sulfur coordinates were then obtained by a consideration of the absolute intensities of those reflections to which the barium atom did not contribute. The various combinations of tetrasulfide group orientations present in Fig. 2 were used in this process. The first successful model gave a value of $R_1 = 0.312$ for all the planes observed in this zone. After six Fourier series refinements, the projection shown in Fig. 3 finally resulted.

The z coordinates were obtained from the (h0 ℓ) data together with the symmetrized (0k ℓ) map of Fig. 4. The coordinates thus found were not very good, for the initial value of R_1 was 0.52. Seven subsequent Fourier series iterations then gave the electron density map in Fig. 5. The (0k ℓ) projection followed from the y and z coordinates already determined, and is given in Fig. 6. During the course of this refinement, it was noticed that the oxygen atoms had become clearly resolved, and inclusion of these atoms reduced R_1 in each zone by 1 to 2 percent.

In the case of the b-axis projection, the experimental arrangement permitted the entire reciprocal layer to be explored by means of MoK α radiation. It is interesting to note that, with Cu radiation, the value of R_1 did not fall below 0.24, whereas substitution of Mo radiation not only added 38 new terms

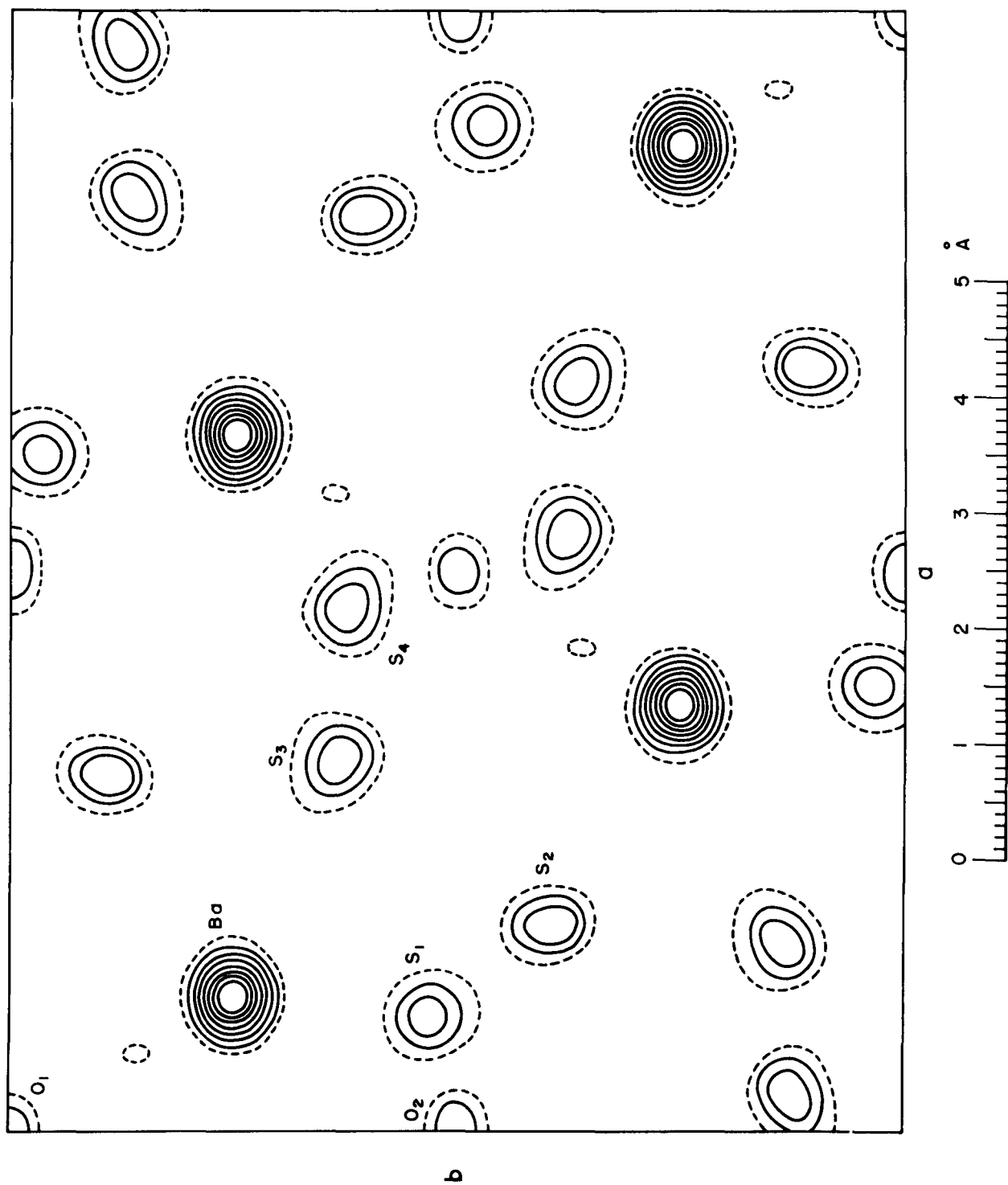


Fig. 3. Projection of the unit cell along the c axis. Each contour for the barium atom represents a density increment of $20e \text{ \AA}^{-2}$, for the sulfur atoms it is $10e \text{ \AA}^{-2}$ and for the oxygen atom it is $5e \text{ \AA}^{-2}$, the 10-electron line being broken.

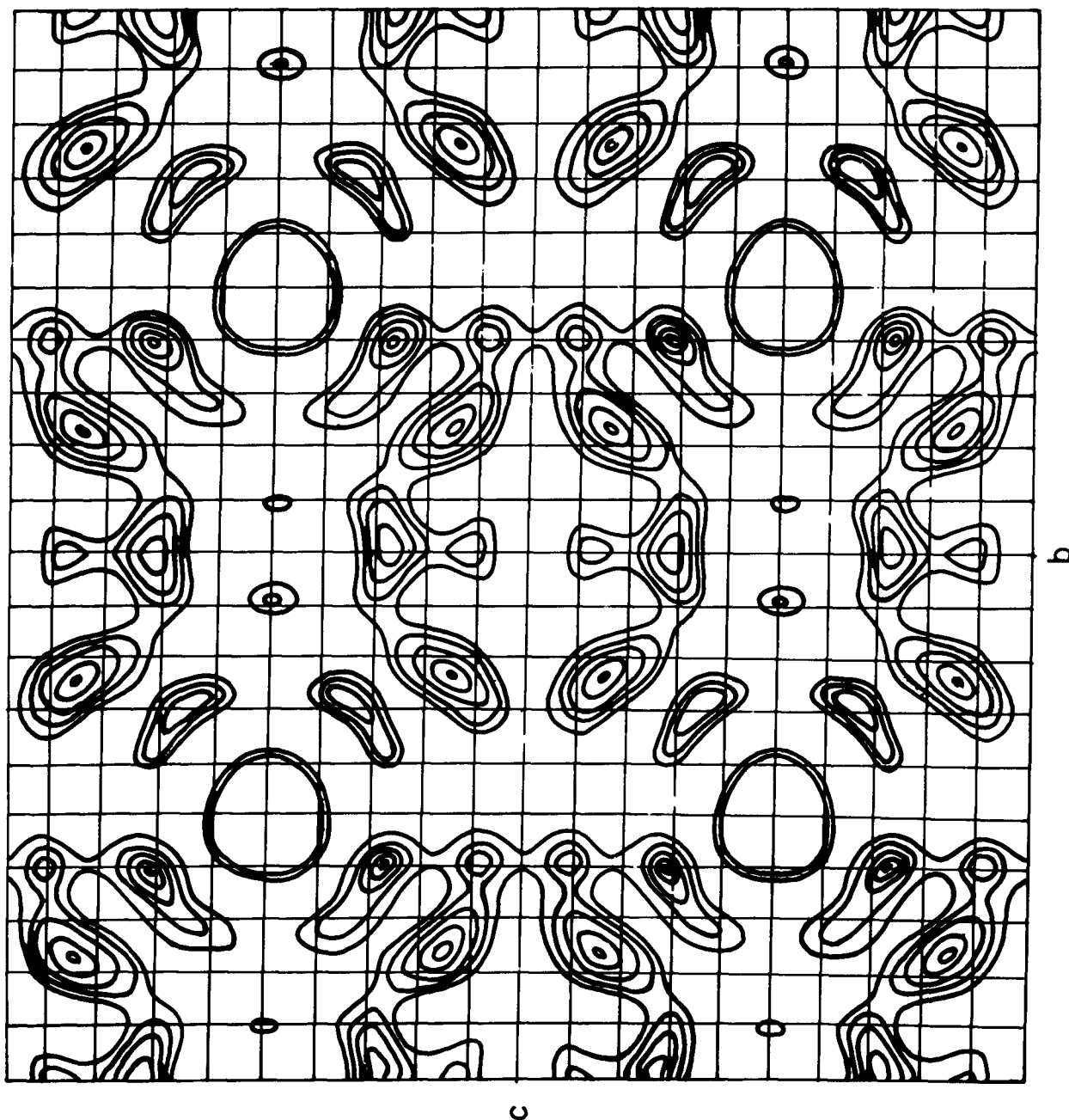


Fig. 4. Symmetrized a-axis projection, based only on the barium atom at $1/4, 1/4$, computed on the X-Ray Analog Computer.

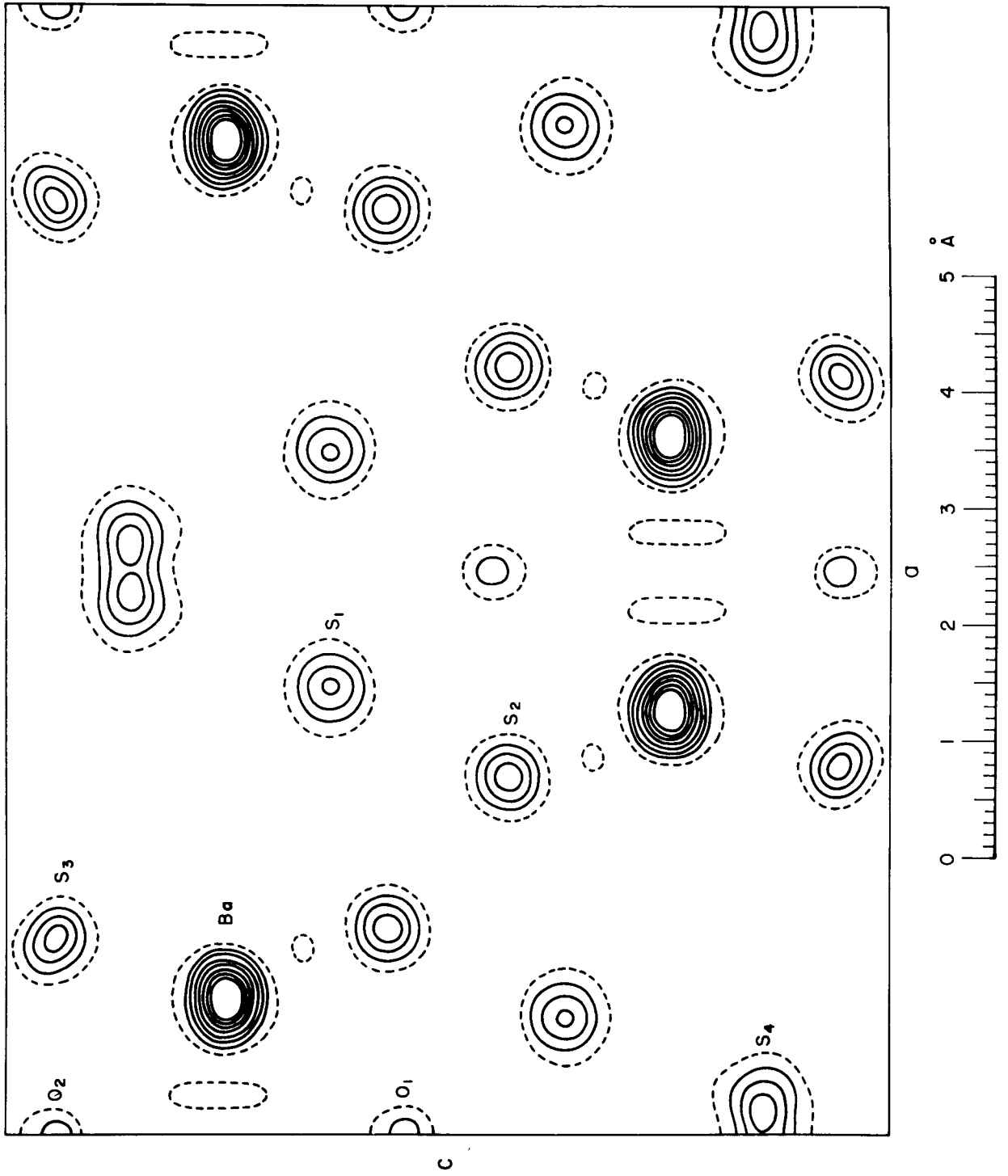


Fig. 5. Normal projection of the unit cell along the b axis. Contour scale as in Fig. 3.

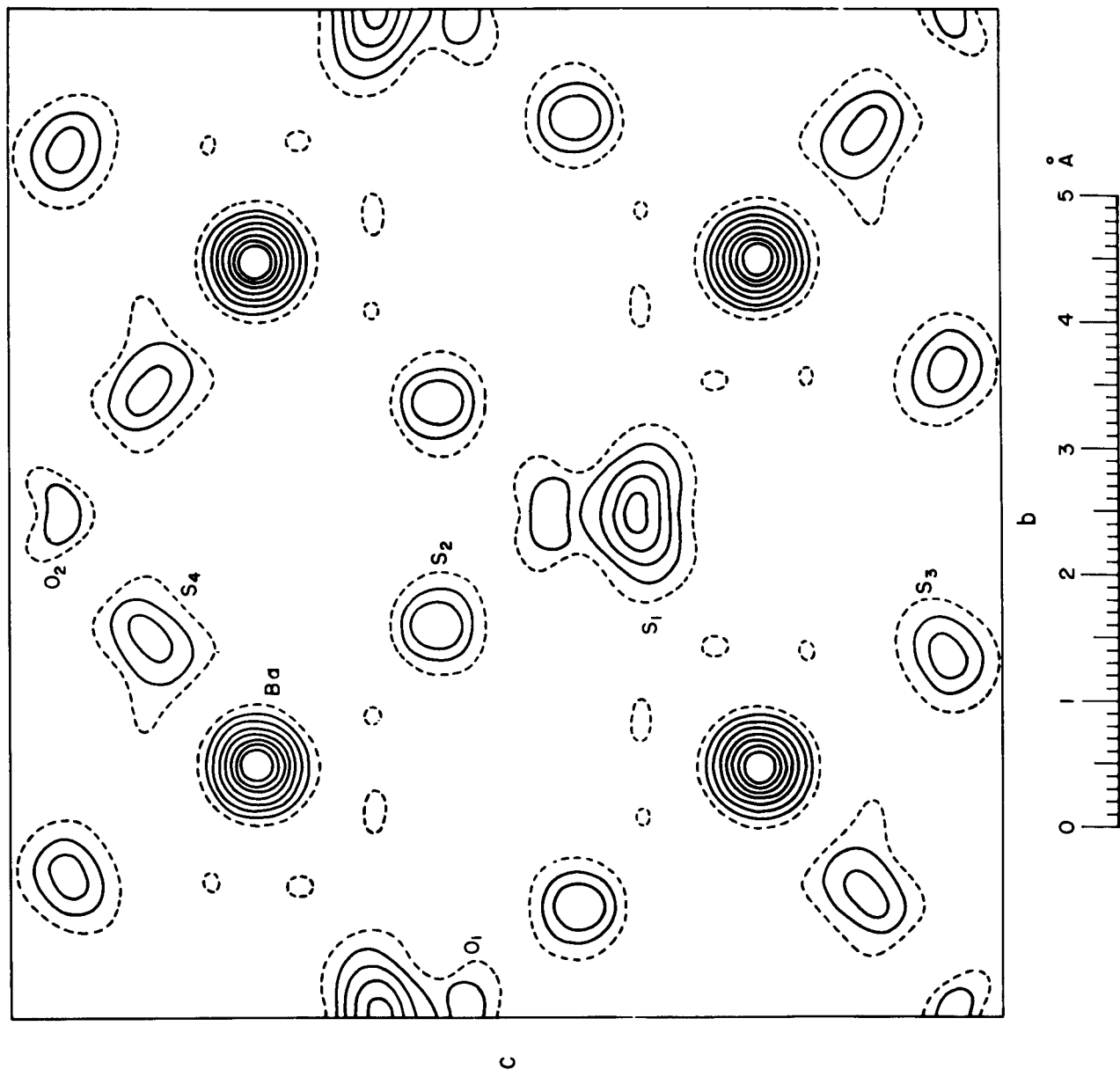


Fig. 6. Normal projection of the unit cell along the *a* axis.
Contour scale as in Fig. 3.

to the series, but also lowered the value of R_1 for the previously observed 92 terms to 0.108. It was then felt that this series was sufficiently complete to be free from appreciable error due to artificial termination. In the other two zones, however, the series was abruptly terminated at $\sin \theta = 0.50$ for MoK α , the limit of the sphere of reflection observable with the precession camera. Hence further refinement was sought by the application of the method of least squares. In using this method, all weights were placed equal to unity, and only the diagonal terms of the matrix solved. Thus expressions of the type

$$\Delta \xi_j = \sum \frac{\partial F_{hkl}}{\partial \xi_j} \cdot \Delta F_{hkl} \div \sum \left[\frac{\partial F_{hkl}}{\partial \xi_j} \right]^2$$

were used. The values of $\Delta \xi_j$ thus obtained were added to the original ξ_j 's and a further cycle of refinement then completed. Three such cycles for the (0k ℓ) data and two for the (hk0) data sufficed to reduce the largest value of $\Delta \xi_s$ to 0.0013 for (0k ℓ) and 0.0009 for (hk0) thus decreasing the value of R_1 by 1.2 and 0.4%, respectively, in the two zones. At this stage, it was thought no further refinement was feasible. No signs changed during the least-squares process.

The final values of R_1 for the principal zones after these processes were completed were 0.110 for (hk0), 0.094 for (0k ℓ), 0.134 for (h0 ℓ), and total $R_1 = 0.115$, based upon 296 observations and 17 parameters.

Atomic coordinates

The atomic positions were taken as coincidental with the center of electron mass in the (h0 ℓ) projection (Fig. 5) for the x and z coordinates. Together with the values derived from the least squares refinement procedures for the groups of x and y, and the y and z coordinates, these results are collected in Table 1. Every atom thus has two independent values for each of its three coordinates, and the weighted mean of these pairs was taken for the final coordinates, having due regard for the previous behavior of that coordinate (e.g., if the coordinate of an atom obtained by one process had not appreciably altered through several

Table 1. Atomic coordinates in $\text{BaS}_4 \cdot \text{H}_2\text{O}$. Origin at 112, plane of $2_1^2 1$.

	x				y				z		
	hk0	h0l	wt. mean	hk0	h0l	wt. mean	hk0	h0l	wt. mean	0kl	wt. mean
Ba	0.1195	0.1196	0.1195	0.2503	0.2498	0.2501	0.2480	0.2474	0.2477		
S ₁	0.1028	0.1052	0.1040	0.4694	0.4723	0.4708	0.6328	0.6346	0.6330		
S ₂	0.1828	0.1813	0.1820	0.3991	0.9670	0.3987	0.4320	0.4313	0.4318		
S ₃	0.3301	0.3304	0.3303	0.3626	0.3596	0.3620	0.9462	0.9439	0.9455		
S ₄	0.4679	0.4667	0.4670	0.3780	0.3774	0.3776	0.1413	0.1426	0.1415		
O ₁	0	0	0	0	0	0	0.4485	0.4473	0.4479		
O ₂	0	0	0	0.5000	0.5000	0.5000	0.9535	0.9553	0.9544		

refinement cycles, whereas that obtained from a different set of data had oscillated, the former value would be favored). A common origin was used in computing the data in each zone, and is explicitly given in the heading of Table 1.

Dimensions in the tetrasulfide ions

In this crystal, there are two crystallographically independent tetrasulfide ions, since the two-fold axes present pass through each ion. The bond lengths and angles of the two ions are given in Table 2, and are also represented in Fig. 7.

Table 2. Dimensions in the tetrasulfide ion.

$S_1 - S_2 = 2.03_2 \overset{\circ}{\text{Å}}$	$S_3 - S_4 = 2.02_1 \overset{\circ}{\text{Å}}$
$S'_1 - S_1 = 2.06_6$	$S'_4 - S_4 = 2.06_8$
$S'_1 S_1 S_2 = 104^\circ 4'$	$S'_4 S_4 S_3 = 104^\circ 54'$
Dihedral angles: $S'_1 S_1 S_2 / S'_1 S_1 S'_2 = 74^\circ 5'$	
$S'_3 S'_4 S_4 / S_3 S_4 S'_4 = 77^\circ 10'$	

Errors in the coordinates

In the analysis of cesium hexasulfide, a variety of ways of estimating the errors in the coordinates were used (Booth, 1945, 1946, 1947, and Cruickshank, 1949). Of these the last method appeared the most satisfactory. In the present study, Cruickshank's method was applied to the (h0l) data. The following relation was used: $\sigma(x) = \frac{\sigma(A_h)}{A_{hh}}$, where $\sigma(A_h) = \frac{2\pi}{aA} \left\{ \sum h^2 \Delta F^2 \right\}^2$, and $A_{hh} = -2pN_j(p/\pi)^{3/2}$, where p is derived by assuming the profile of the atomic peaks in the electron density map is of the form $\exp(-pr^2)$, using Cruickshank's notation. The values of p obtained were 14.6, 10.4 and 5.4 for barium, sulfur and oxygen, respectively. These values are higher than usual, probably because of the small temperature

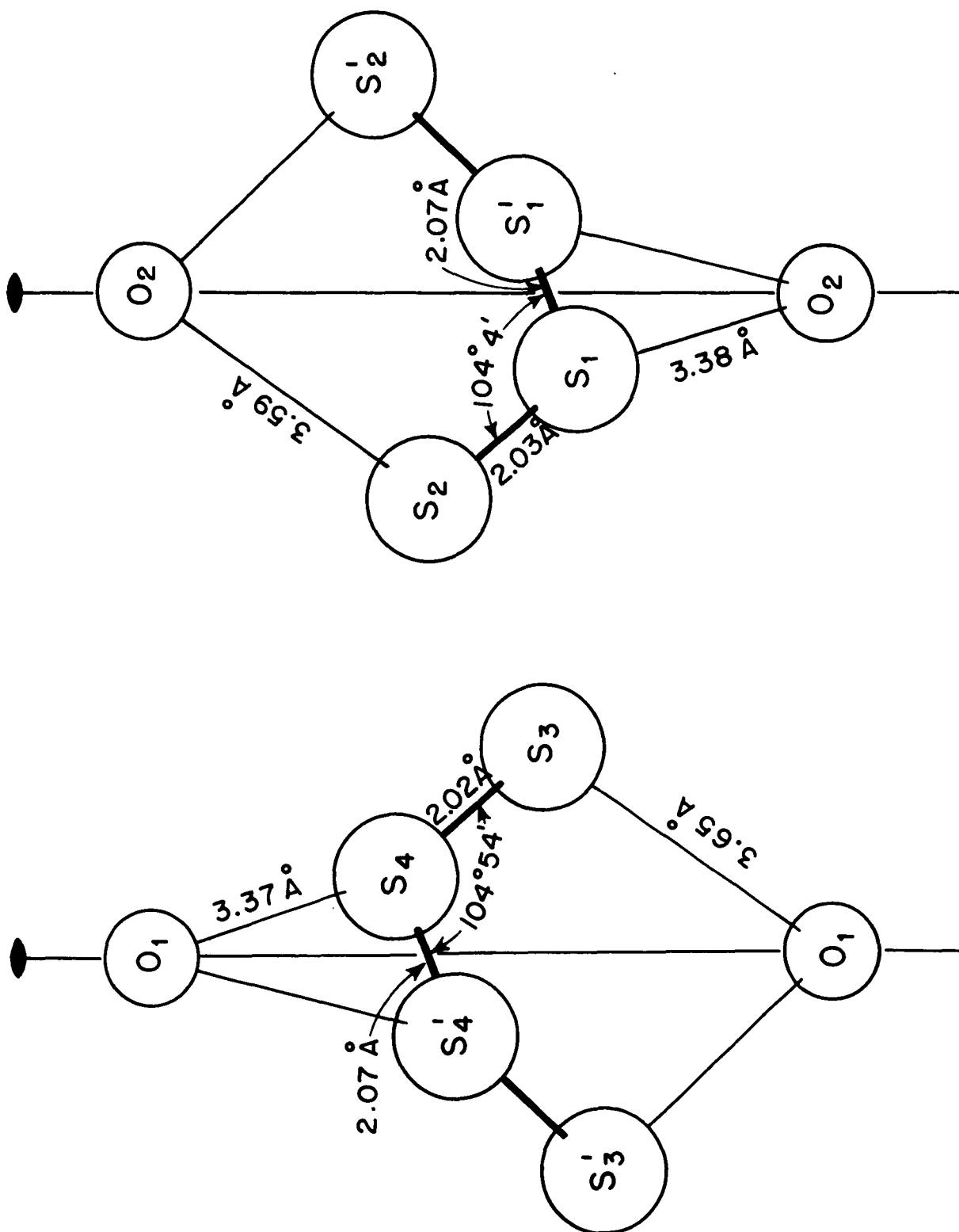


Fig. 7. Dimensions in the groups lying on the 2-fold axes.

Table 3. Errors in the coordinates.

	x		y		z		Standard deviation
	L.S.* σ_{hk0}	F.S.* σ_{h0l}	L.S. σ_{hk0}	L.S. σ_{0kl}	L.S. $\sigma_{0k l}$	F.S. σ_{h0l}	
Ba	0.0039 Å	0.0005 Å	0.0047 Å	0.0058 Å	0.0047 Å	0.0005 Å	0.010 Å
S ₁	0.016	0.005	0.016	0.016	0.015	0.005	0.027
S ₂	0.017	0.005	0.017	0.021	0.017	0.005	0.029
S ₃	0.017	0.005	0.016	0.018	0.018	0.005	0.026
S ₄	0.017	0.005	0.016	0.019	0.017	0.005	0.027
O ₁	0	0	0	0	0.067	0.028	0.07
O ₂	0	0	0	0	0.066	0.026	0.07

factor and the extent of the series, which effectively sharpens these series very considerably. Hence, $\sigma(A_h) = 5.37$ and $\sigma(A_l) = 4.93 e \text{ Å}^{-3}$. The standard deviation is then $[\sigma(x)^2 + \sigma(y)^2 + \sigma(z)^2]^{1/2}$.

The error in the coordinates may also be calculated from the least-squares data by a standard procedure. Here,

$$\sigma(x_j) = \left\{ \frac{\sum (\Delta F_{hkl})^2}{(m-s) \sum \left[\frac{\partial F_{hkl}}{\partial x_j} \right]^2} \right\}^{1/2},$$

where m is the number of observational equations and s is the number of parameters. The errors thus computed are collected in Table 3. These standard deviations may be compared with the differences between those bonds and angles in the two tetrasulfide ions which chemically should be identical, but crystallographically are not required to be the same. The maximum difference in length observed is 0.01 Å and in angle is 1°, so it appears likely in this analysis that the calculated standard deviations in Table 3 for the sulfur atoms, if in error at all, are on the high side.

* L.S., least squares; F.S., Fourier series.

Table 4. Interatomic distances less than 4.0 \AA .

$\text{Ba} - \text{O}_2 = 2.79_6 \text{ \AA}$	$\text{Ba} - \text{O}_1 = 2.79_6 \text{ \AA}$
$\text{S}_1 - \text{O}_2 = 3.37_7$	$\text{S}_4 - \text{O}_1 = 3.36_9$
$\text{S}_2 - \text{O}_2 = 3.58_6$	$\text{S}_3 - \text{O}_1 = 3.65_1$
$\text{S}_1 - \text{S}_3 = 3.38_9$	$\text{Ba} - \text{S}_2 = 3.21_1$
$\text{Ba} - \text{S}_3 = 3.18_0$	$\text{Ba} - \text{S}_2^* = 3.37_1$
$\text{Ba} - \text{S}_3'^* = 3.30_4$	$\text{Ba} - \text{S}_2' = 3.46_2$
$\text{Ba} - \text{S}_3^* = 3.48_7$	$\text{Ba} - \text{S}_1 = 3.49_2$
$\text{Ba} - \text{S}_4'^* = 3.52_8$	

Interatomic distances

The closest approach distances, less than 4 \AA , among the barium and the tetrasulfide ions and the water molecule are listed in Table 4. The primed atoms are related to the unprimed by the two-fold axes, and the starred atoms are related to the unprimed by the relation $(xyz)^* = (1/2 - x, 1/2 + y, \bar{z})$. A clinometric view of the structure is shown in Fig. 8.

Discussion

As in the case of cesium hexasulfide, this study confirms the view that the polysulfide group is nonbranched and noncoplanar, although here the tetrasulfide ion possesses C_2 symmetry. In this crystal the barium atom is surrounded by nine other atoms at distances less than 4 \AA apart. Two of these distances are between oxygen and barium, and are equal at 2.80 \AA . This compares very closely with the ionic separation between barium and oxygen in BaO of 2.76 \AA . The shortest barium-sulfur contact is 3.18 \AA , which may be compared with the corresponding distance in BaS of 3.17 \AA . It is thus entirely likely that the barium atom is completely ionized, and that the tetrasulfide group, in consequence, possesses a two-electron charge. If now it is assumed that the

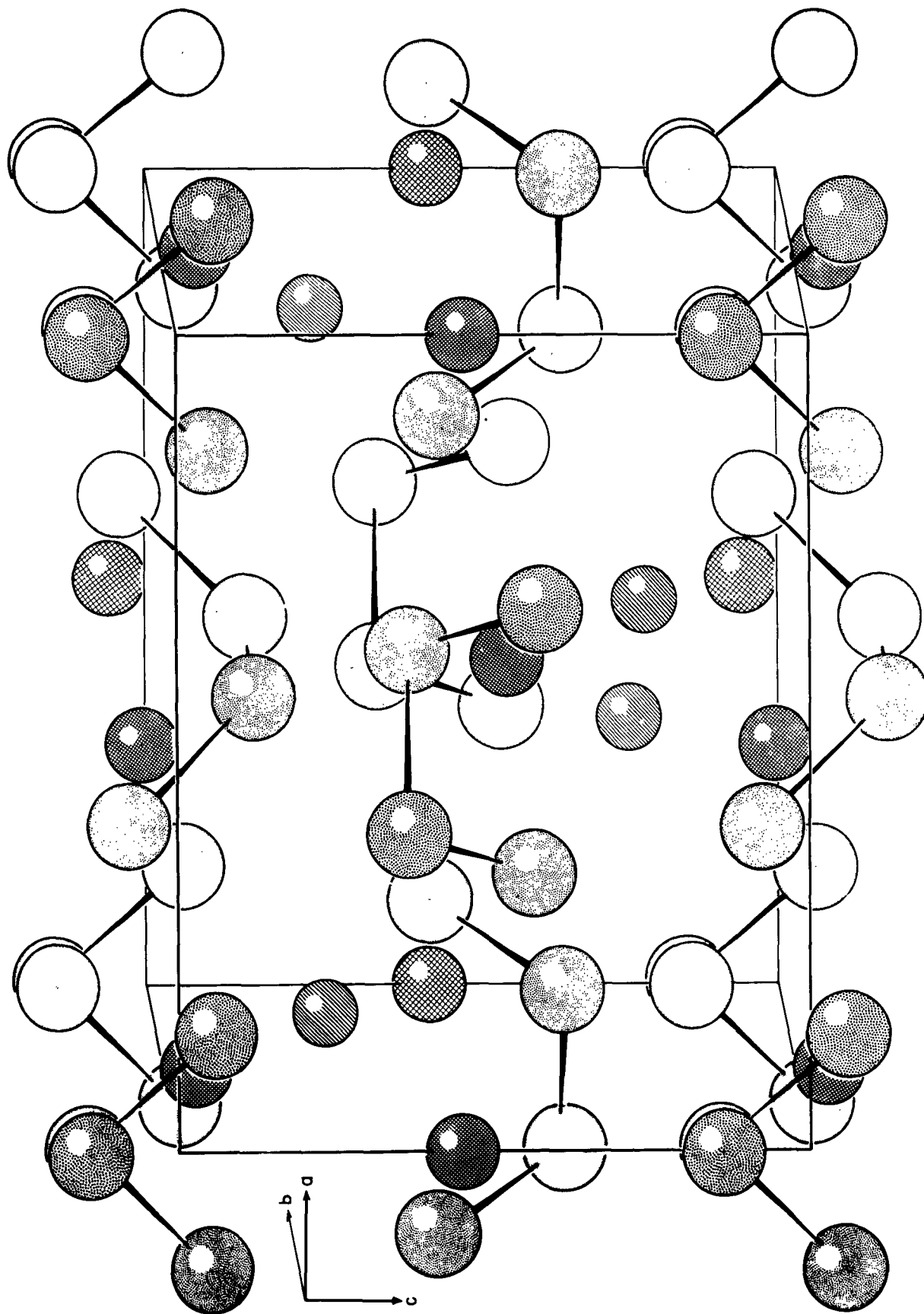


Fig. 8. A clinometric view of the structure, showing the outlines of one unit cell. The hatched circles represent barium atoms, the shaded circles are for sulfur atoms and the cross-hatched circles are the oxygen atoms.

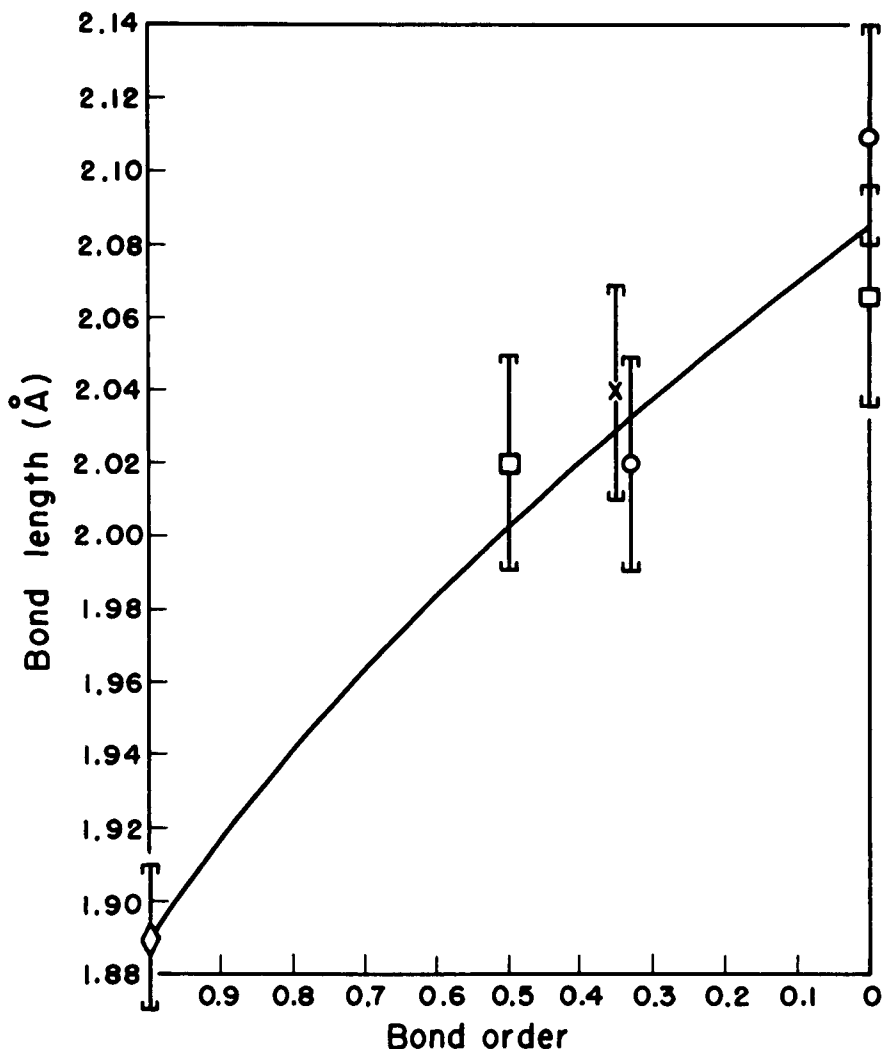


Fig. 9. Relation between interatomic distance and bond order in the sulfur-sulfur bond. The squares represent $BaS_4 \cdot H_2O$ data, the circles are for Cs_2S_6 , the cross is for thiophene, and the diamond is for S_2 .

longer central bond in the tetrasulfide ion is a single sulfur-sulfur bond, i. e., with order zero, then each of the remaining two bonds will be enriched by one extra electron, and will hence possess a bond order of 0.5. The bond lengths corresponding to these bond orders, together with the similar data found in the cesium hexasulfide study, are combined in Fig. 9, in which each length is given, together with its estimated standard error. Further, continuing the argument of

Evans and de Heer (1949), a bond order vs. length curve for carbon-sulfur may be established, in which a straight line relation is assumed to exist between C-S, bond order 0 and length 1.79 \AA , and C=S, order 1 and length 1.60 \AA . The C-S distance found in thiophthene (Cox, Gillot and Jeffrey, 1949) of 1.73 \AA thus corresponds to a bond order of 0.35. Applying the standard carbon-carbon bond order vs. length curve, and the additivity of these covalent distances,* the sulfur-sulfur distance corresponding to order 0.35 is 2.04 \AA . This point, assuming an error of $\pm 0.03 \text{ \AA}$ to account for the approximations in this treatment, may be seen to fit quite well in Fig. 9.

The stability of this structure appears principally due to ionic binding, with barium-oxygen contacts occurring helically through the crystal. An interesting feature is the relation of the water group to the tetrasulfide ions. Both groups lie on two-fold symmetry axes, and each tetrasulfide ion has two water molecules as neighbors, unsymmetrically arrayed on either side (Fig. 7). The closest oxygen-sulfur approach is 3.38 \AA which is rather more than the sum of the ionic radii. A possibility of interest is that this piezoelectric crystal might become ferroelectric at a different temperature by inducing a cooperative movement of the water or tetrasulfide groups, relative to the barium ions. Efforts are now being made to grow a crystal large enough to examine this possibility experimentally.

Experimental

The orange needle crystals of barium tetrasulfide monohydrate were prepared by the method of Robinson and Scott (1931). They are quite stable in contact with the atmosphere, in contrast with cesium hexasulfide. The largest of the three crystals examined had dimensions $0.25 \times 0.42 \times 0.70 \text{ mm}$ and the smallest $0.16 \times 0.16 \times 0.45 \text{ mm}$.

Weissenberg and precession cameras were employed in this study, using

* Carbon and sulfur have nearly equal electronegativities.

only MoK α ($\lambda = 0.7107 \text{ \AA}$) radiation for the final determination of the atomic coordinates. A new Weissenberg camera was used, built in this laboratory, which has a 3 1/2 inch dia. film holder, to spread the reflections obtained with Mo radiation, and hence make it easier to measure the intensities. The beam stop was designed so that the 1st order reflection of a 10 \AA axis could be observed with this radiation. The film holder had a section subtending ca. 90° removed from the back reflection region on the lower side, to let it slip over the cylindrically split and hinged layer line screen, a modification similar to that previously described by Abrahams and Lipscomb (1952), which enables the camera to be used conveniently at low or elevated temperatures. The precession angle was 30° with a crystal-screen distance of 5.5 cm. The intensities were measured visually, using a multiple exposure technique for correlating the weak and strong reflections. Absorption corrections were not made since the crystals were small and very regular in shape. The ratio of the strongest intensity to the weakest in each of the three zones studied was about 600 to 1, a small ratio considering that exposures of 45 h. were made with the largest crystal.

The excellent agreement obtained between observed and calculated structure factors did not appear to warrant the use of a correction for the anomalous dispersion of the K and L electrons, especially as the latter is not well known for barium. A study in this laboratory is under way to measure this dispersion experimentally for several atoms with atomic number about 50.

The values for the measured structure factors were derived from the intensities in the usual way, applying Waser's (1951) Lorenz and polarization correction to the intensities in the zero layers measured on the precession camera. The calculated structure factors were based on the atomic coordinates in Table 1, and both sets of structure factors are assembled in Table 5.

Table 5. Measured and calculated values of the structure factors.

hkl	F _{meas}	F _{calc}	hkl	F _{meas}	F _{calc}	hkl	F _{meas}	F _{calc}
200	51	+ 41	810	68	+ 73	540	< 13	+ 16
400	173	- 178	910	41	- 30	640	83	- 81
600	46	+ 32	1010	92	- 101	740	35	- 36
800	81	+ 86	1110	37	- 28	840	145	+ 147
1000	57	+ 51	1210	< 15	- 15	940	< 15	+ 6
1200	53	- 55	1310	15	+ 10	1040	53	+ 56
1400	68	- 75	120	27	+ 21	1140	15	+ 14
1600	40	+ 45	220	34	+ 18	1240	63	- 68
020	120	- 114	320	55	+ 47	150	41	- 32
040	98	+ 98	420	141	+ 146	250	190	- 191
060	121	- 111	520	17	+ 17	350	33	- 29
080	150	+ 154	620	25	+ 22	450	< 14	- 17
0100	72	- 70	720	14	+ 17	550	14	+ 23
001	4	+ 2	820	85	- 89	650	96	+ 100
002	120	- 118	920	38	+ 33	750	< 15	- 7
003	7	- 1	1020	< 15	- 1	850	15	+ 10
004	93	+ 93	1120	< 15	+ 5	950	< 15	- 12
005	30	+ 32	1220	66	+ 74	1050	71	- 71
006	135	- 136	130	84	- 67	1150	14	+ 14
007	12	- 3	230	216	+ 204	1250	34	- 48
008	82	+ 83	330	11	+ 12	160	< 14	+ 4
009	13	- 3	430	28	- 18	260	< 14	+ 10
0010	109	- 122	530	12	+ 9	360	< 14	+ 3
0011	20	- 22	630	77	- 75	460	120	+ 104
0012	33	+ 39	730	< 14	- 9	560	14	- 15
0013	< 17	+ 5	830	15	+ 17	660	20	+ 16
0014	18	- 19	930	< 15	+ 1	760	47	- 45
110	< 6	- 5	1030	61	+ 66	860	72	- 63
210	127	- 136	1130	< 15	- 6	960	29	- 29
310	60	+ 49	1230	49	+ 44	1060	20	- 20
410	63	- 57	140	12	- 14	1160	12	+ 9
510	44	+ 38	240	50	+ 38	170	20	+ 24
610	154	+ 173	340	30	+ 28	270	72	+ 52
710	13	+ 17	440	151	- 147	370*	15	- 15

* See last page of Table 5.

Table 5 (continued)

hkl	F _{meas}	F _{calc}	hkl	F _{meas}	F _{calc}	hkl	F _{meas}	F _{calc}
380	< 15	+ 11	1201	< 14	0	1303	60	+ 73
480	80	- 77	1301	43	- 52	1403	< 15	+ 1
580	15	- 23	1401	< 15	+ 3	104	< 8	+ 4
680	15	+ 14	1501	17	+ 28	204	29	- 23
780	< 15	+ 6	1601	< 17	- 11	304	15	+ 17
880	60	+ 62	1701	36	+ 56	404	125	- 125
980	22	- 20	102	8	- 6	504	< 10	+ 10
190	< 15	+ 10	202	52	- 41	604	10	- 11
290	81	- 89	302	61	- 49	704	11	+ 12
390	20	+ 26	402	152	+ 153	804	97	+ 88
490	14	- 19	502	81	- 63	904	13	- 18
590	< 14	- 6	602	88	+ 79	1004	< 13	+ 18
690	83	+ 90	702	< 10	+ 5	1104	< 14	- 10
790	< 12	+ 3	802	131	- 128	1204	51	- 54
890	33	+ 49	902	24	+ 28	1304	< 16	+ 13
1100	< 14	+ 22	1002	13	- 23	1404	< 16	- 7
2100	< 14	- 3	1102	< 13	+ 16	105	189	+ 189
3100	19	+ 23	1202	78	+ 92	205	< 9	- 10
4100	73	+ 85	1302	< 15	+ 13	305	104	- 108
5100	< 11	+ 3	1402	18	+ 21	405	22	- 25
6100	27	+ 23	1502	< 17	- 5	505	64	- 57
1110	12	- 14	1602	20	- 32	605	< 12	- 5
2110	60	+ 68	103	121	- 113	705	64	+ 65
101	106	+ 106	203	34	- 29	805	< 13	+ 4
201	42	+ 26	303	52	+ 42	905	56	+ 62
301	163	- 156	403	61	- 44	1005	14	+ 18
401	37	+ 27	503	156	+ 176	1105	< 14	- 2
501	91	- 88	603	17	- 15	1205	< 15	0
601	30	+ 27	703	53	- 46	1305	60	- 75
701	82	+ 69	803	< 11	+ 6	1405	< 17	- 9
801	< 11	- 1	903	115	- 122	106	< 12	+ 14
901	68	+ 67	1003	13	+ 17	206	30	+ 28
1001	39	- 35	1103	59	+ 62	306	15	+ 12
1101	19	- 20	1203	17	+ 21	406	113	+ 116

Table 5 (continued)

hkl	F _{meas}	F _{calc}	hkl	F _{meas}	F _{calc}	hkl	F _{meas}	F _{calc}
506	28	+ 27	1108	< 17	+ 17	4012	44	- 49
606	17	- 9	1208	48	- 69	5012	17	+ 22
706	13	+ 18	109	13	+ 25	6012	17	- 10
806	57	- 61	209	< 14	- 3	7012	17	- 6
906	23	- 23	309	39	- 45	8012	29	+ 37
1006	29	- 29	409	< 14	- 1	1013	35	+ 40
1106	< 15	- 18	509	54	- 61	2013	17	+ 17
1206	34	+ 41	609	< 15	- 5	3013	17	- 14
1306	< 17	0	709	33	+ 40	4013	18	- 5
1406	< 17	+ 25	809	< 16	+ 5	5013	44	- 53
107	56	- 51	909	38	+ 53	6013	18	- 10
207	< 12	+ 10	1009	< 17	+ 7	7013	18	+ 17
307	44	+ 47	1109	28	- 26	1014	18	- 1
407	43	+ 49	1209	< 17	- 11	2014	18	0
507	75	+ 85	1010	< 15	+ 15	3014	18	+ 4
607	18	+ 24	2010	15	- 12	4014	28	+ 38
707	27	- 35	3010	20	- 27	011	< 5	+ 3
807	14	- 24	4010	62	+ 71	021	67	- 52
907	61	- 67	5010	15	- 15	031	50	+ 42
1007	< 15	- 12	6010	15	- 7	041	47	- 44
1107	31	+ 41	7010	16	0	051	42	+ 42
1207	< 16	- 8	8010	44	- 51	061	15	+ 20
1307	34	+ 50	1011	39	- 58	071	< 12	+ 4
1407	< 18	- 3	2011	16	- 3	081	12	+ 23
108	< 12	- 9	3011	55	+ 66	091	12	- 21
208	42	+ 44	4011	16	- 4	0101	11	- 22
308	18	- 22	5011	40	+ 38	0111	< 8	- 7
408	79	- 87	6011	16	- 20	012	58	- 47
508	< 13	+ 3	7011	17	- 29	022	175	+ 195
608	52	- 59	8011	17	+ 3	032	61	- 50
708	< 14	- 4	9011	17	- 35	042	171	- 175
808	90	+ 97	1012	16	- 1	052	40	- 32
908	< 15	- 6	2012	17	- 5	062	125	+ 120
1008	18	+ 25	3012	17	+ 17	072	< 11	- 12

Table 5 (continued)

hkl	F _{meas}	F _{calc}	hkl	F _{meas}	F _{calc}	hkl	F _{meas}	F _{calc}
082	74	- 74	015	< 9	- 5	067	12	- 20
092	11	- 5	025	14	+ 11	077	< 11	+ 10
0102	72	+ 72	035	56	- 56	087	< 9	+ 3
0112	< 6	+ 7	045	11	+ 19	018	25	- 25
013	< 7	+ 2	055	10	- 20	028	78	- 80
023	31	+ 30	065	< 10	- 13	038	< 12	- 6
033	18	+ 14	075	25	+ 31	048	111	+ 111
043	41	+ 34	085	< 11	+ 5	058	< 12	+ 6
053	41	+ 40	095	< 10	+ 3	068	62	+ 68
063	33	+ 30	0105	< 6	+ 2	078	< 9	- 5
073	< 12	+ 24	016	62	+ 61	019	< 12	+ 13
083	12	- 14	026	113	+ 117	029	< 12	- 10
093	18	- 22	036	32	- 25	039	25	+ 21
0103	< 10	- 12	046	84	- 87	049	< 12	+ 15
014	56	+ 54	056	25	- 28	059	11	+ 10
024	170	- 176	066	102	+ 98	069	29	- 27
034	64	- 54	076	18	+ 23	0110	38	- 35
044	141	+ 134	086	79	- 78	0210	57	+ 61
054	55	- 51	096	< 7	+ 11	0310	< 11	+ 2
064	114	- 106	017	< 11	- 3	0410	59	- 48
074	12	+ 16	027	< 11	+ 3	0111	< 9	+ 12
084	64	+ 69	037	20	- 22	0211	< 8	+ 25
094	16	+ 15	047	49	- 48	0311	< 6	+ 1
0104	76	- 73	057	< 12	- 9			

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470	15	+ 15	770	15	+ 9	1070	65	+ 69
570	21	+ 30	870	20	- 28	180	42	+ 43
670	100	- 101	970	19	- 24	280	15	+ 19

The structure factor and the least-squares calculations were computed on punched card machines with 4-figure accuracy. The Fourier series were all summed using Beevers-Lipson strips, sampling the electron densities at

intervals of 12° along each axis. The positions of the contour lines were obtained from the summation totals by careful graphical interpolation on a scale of 5 cm to 1 \AA , in directions parallel with each axis.

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